

AD-A227 802

OFFICE OF NAVAL RESEARCH

Contract No. N00014-83-K-0611

R & T Code 4135003-1

Replaces old

Task No. NR 053-842

TECHNICAL REPORT NO. UK/DC/TR-32

DTIC FILE COPY

Tin(II) Poly(1-pyrazolyl)borates

by

M. N. Hansen, K. Niedenzu, J. Serwatowska, J. Serwatowski, and K. R. Woodrum

Prepared for publication in

INORGANIC CHEMISTRY

University of Kentucky
Department of Chemistry
Lexington, KY 40506

October 1990

Reproduction in whole or in part is
permitted for any purpose of the United States Government

This document has been approved for public
release and sale; its distribution is unlimited

2

DTIC FILE COPY	
Replaces old	
Task No. NR 053-842	
TECHNICAL REPORT NO. UK/DC/TR-32	
Tin(II) Poly(1-pyrazolyl)borates	
by	
M. N. Hansen, K. Niedenzu, J. Serwatowska, J. Serwatowski, and K. R. Woodrum	
Prepared for publication in	
INORGANIC CHEMISTRY	
University of Kentucky	
Department of Chemistry	
Lexington, KY 40506	
October 1990	
Reproduction in whole or in part is	
permitted for any purpose of the United States Government	
This document has been approved for public	
release and sale; its distribution is unlimited	



DTIC
ELECTE
OCT 16 1990
D

REPORT DOCUMENTATION PAGE				Form Approved OASD No. 0704-0100	
1a. REPORT SECURITY CLASSIFICATION unclassified			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT prepared for publication in INORGANIC CHEMISTRY		
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UK/DC/TR-32			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION Department of Chemistry University of Kentucky		6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research		
6c. ADDRESS (City, State, and ZIP Code) Lexington, KY 40506-0055			7b. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000		
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) 800 North Quincy Street Arlington, VA 22217-5000			10. SOURCE OF FUNDING NUMBERS		
		PROGRAM ELEMENT NO.	PROJECT NO.	R & T code 4135003-1	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) TIN(II) POLY(1-PYRAZOLYL)BORATES (unclassified)					
12. PERSONAL AUTHOR(S) M. N. Hansen, K. Niedenzu, J. Serwatowska, J. Serwatowski, K. R. Woodrum					
13a. TYPE OF REPORT interim technical		13b. TIME COVERED FROM TO		14. DATE OF REPORT (Year, Month, Day) 90/10	
15. PAGE COUNT 12					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP	poly(1-pyrazolyl)borates		
			tin(II) complexes		
			NMR studies		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A series of Sn(II) poly(1-pyrazolyl)borates of the types L_2Sn where $L = [B(pz)_4]^-$ (1), $[B(pz')_4]^-$ (2), $[HB(pz)_3]^-$ (3), $[R_2B(pz)_2]^-$ (R = H (5) or C_6H_5 (6)), or $[H_2B(pz)_2]^-$ (7) (Hpz = pyrazole, Hpz' = 3-methylpyrazole) and $LSnCl$ where $L = [B(pz')_4]^-$ (8), $[R_2B(pz)_2]^-$ (R = H (10) or C_6H_5 (11)) or $[H_2B(pz)_2]^-$ (12) have been prepared and characterized by NMR data. The observed ^{119}Sn chemical shifts correlate with the assumed coordination sphere of the Sn(II).					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. Kurt Niedenzu			22b. TELEPHONE (Include Area Code) (606) 257-7073		22c. OFFICE SYMBOL

Tin(II) Poly(1-pyrazolyl)borates

M. N. Hansen, K. Niedenzu,* J. Serwatowska, J. Serwatowski, and K. R. Woodrum

Received

A series of Sn(II) poly(1-pyrazolyl)borates of the types L_2Sn where $L = [B(pz)_4]^-$ (1), $[B(pz')_4]^-$ (2), $[HB(pz)_3]^-$ (3), $[R_2B(pz)_2]^-$ ($R = H$ (5) or C_6H_5 (6)), or $[H_2B(pz')_2]^-$ (7) ($Hpz =$ pyrazole, $Hpz' =$ 3-methylpyrazole) and $LSnCl$ where $L = [B(pz')_4]^-$ (8), $[R_2B(pz)_2]^-$ ($R = H$ (10) or C_6H_5 (11)) or $[H_2B(pz')_2]^-$ (12) have been prepared and characterized by NMR data. The observed ^{119}Sn chemical shifts correlate with the assumed coordination sphere of the Sn(II).

Introduction

Ever since their first preparation¹ poly(1-pyrazolyl)borates, $M[(pz)_{4-n}BR_n]$ ($M =$ alkali metal, $Hpz =$ pyrazole or C-substituted derivative thereof, $R =$ non-coordinating substituent, $n = 0, 1, 2$), have found extensive use as chelating ligands in transition metal chemistry.² However, studies of the poly(1-pyrazolyl)borate chemistry of main group elements have been rather limited. Only most recently have some characterized poly(1-pyrazolyl)borates of main group (other than alkali and alkaline earth) metals become available. The data include four (somewhat contradictory) reports on tin(IV)³⁻⁶ and one on tin(II) derivatives;⁷ silicon or germanium poly(1-pyrazolyl)borates have not yet been reported.

In an extension of recent studies on the interaction of boron compounds with poly(1-pyrazolyl)borates, the synthesis and characterization of other main group element derivatives of the latter is currently being investigated. The present report describes a study of a series of Sn(II) poly(1-pyrazolyl)borates. (15)

Experimental Section

Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, NY. Melting points (uncorrected) were determined on a Mel-Temp block.

NMR spectra were recorded for solutions in CDCl_3 (unless otherwise noted) on a Varian VXR-400 (^{11}B , ^{119}Sn , variable temperature, high-resolution) or GEMINI-200 (^1H , ^{13}C) instrument. Chemical shift data are given in ppm with positive values indicating downfield from the reference (internal $(\text{CH}_3)_4\text{Si}$ for ^1H and ^{13}C NMR, external $(\text{C}_2\text{H}_5)_2\text{O}\cdot\text{BF}_3$ for ^{11}B NMR, external $(\text{CH}_3)_4\text{Sn}$ for ^{119}Sn NMR); s = singlet, d = doublet, t = triplet, q = quartet, m = unresolved multiplet, and an asterisk denotes a broad signal. Coupling constants J are given in hertz. ^{13}C NMR spectra were recorded in the proton decoupled mode.

All nonreferenced reagents were obtained from Aldrich Chemical Co., Milwaukee, WI, and used as received.

$\text{Na}[\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ (Hpz = pyrazole) was prepared by the previously described reaction of $\text{Na}[\text{B}(\text{C}_6\text{H}_5)_4]$ with Hpz .⁸ After extensive purification, ultimately by subliming off traces of adhering Hpz , the pure compound has a mp 284–287 °C. NMR data: $\delta(^1\text{H})$ 7.52 (1 H, d, $J = 2.2$), 7.41 (1 H, d, $J = 1.7$), 7.2 (3 H, m), 6.95 (2 H, m), 6.20 (1 H, unsym t = two overlapping d); $\delta(^{11}\text{B})$ 1.3 (s, $h_{1/2} = 325$ Hz).

$[\text{B}(\text{pz})_4]_2\text{Sn}$ (1). A mixture of 0.94 g (5 mmol) of SnCl_2 , 3.15 g (10 mmol) of $\text{K}[\text{B}(\text{pz})_4]$,¹ and 50 mL of methylene chloride was stirred at room temperature for 5 h. The mixture was filtered and solvent was evaporated from the clear filtrate under reduced pressure to leave 3.2 g (94%) of crude product. It was recrystallized from toluene to give a material of mp 208–210 °C. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{B}_2\text{N}_{16}\text{Sn}$ ($M_r = 676.5$): C, 42.57; H, 3.58; B, 3.20; N, 33.11; Sn, 17.54. Found: C, 43.15; H, 3.50; B, 3.20; N, 33.37; Sn, 17.55.

NMR data: $\delta(^1\text{H})$ 7.63 (1 H, unresolved d), 7.26 (1 H, d, $J = 2.4$), 6.32 (1 H, unsym t = two overlapping d, $J = \text{ca. } 1.9$); $\delta(^{11}\text{B})$ 0.4 (s, $h_{1/2} = 16$ Hz); $\delta(^{13}\text{C})$ 142.2, 135.9, 106.5; $\delta(^{119}\text{Sn})$ -744 (s, $h_{1/2} = 50$ Hz). Solution in CD_2Cl_2 : $\delta(^1\text{H})$ 7.62 (1 H, d, $J = 1.3$), 7.27 (1 H, d, $J = 2.1$), 6.32 (1 H, unsym t = two overlapping d, $J = \text{ca. } 2.1$); at -85 °C: 7.93 (1 H), 7.59 (3 H), 7.40 (3 H), 6.81 (1 H), 6.38 (4 H).

[B(pz')₄]₂Sn (2, Hpz' = 3-methylpyrazole) was obtained from the reaction of 0.33 g (1.74 mmol) of SnCl₂ with 1.30 g (3.48 mmol) of K[B(pz')₄]⁹ (30 mL of methylene chloride, 4 h stirring). The crude material was obtained in quantitative yield; it was washed with cyclohexane to give a product of mp 176–180 °C. Anal. Calcd for C₃₂H₄₀B₂N₁₆Sn (*M_r* = 788.6): C, 48.69; H, 5.11; B, 2.75; N, 28.40; Sn, 15.05. Found: C, 47.15; H, 4.70; B, 3.50; N, 26.99; Sn, 14.84.

NMR data: δ(¹H) 7.4* (s) + 7.2* (s) (1 H total, ratio 1:3), 6.05 (1 H, d, *J* = 1.7), 2.3* (s) + 2.1* (s) (3 H total, ratio 1:3); δ(¹¹B) −0.8 (s, *h*_{1/2} = 30 Hz); δ(¹³C) 151.8, 136.9, 106.5, 13.1; δ(¹¹⁹Sn) −808 (s, *h*_{1/2} = 50 Hz). At 50 °C: δ(¹H) 7.2* (1 H, s), 6.05 (1 H, d, *J* = 1.7), 2.1* (3 H, s).

[B(pz')₄]SnCl (8) was prepared from 0.50 g (2.64 mmol) of SnCl₂ and 0.99 g (2.64 mmol) of K[B(pz')₄]⁹ (30 mL of methylene chloride, 1 h stirring) in essentially quantitative yield. The crude material was washed with cyclohexane to give a product of mp 165–169 °C dec. Anal. Calcd for C₁₆H₂₀BClN₈Sn (*M_r* = 489.1): C, 39.25; H, 4.12; B, 2.21, Cl, 7.26; N, 22.90; Sn, 24.26. Found: C, 39.27; H, 4.11; B, 2.34; Cl, 7.65; N, 22.40; Sn, 24.02.

NMR data: δ(¹H) 7.51* (1 H, s), 6.08* (1 H, s), 2.51 (3 H, s); δ(¹¹B) −1.3 (s, *h*_{1/2} = 35 Hz); δ(¹³C) 151.7, 136.6, 106.6, 13.7; δ(¹¹⁹Sn) −533 (s, *h*_{1/2} = 230 Hz). At −70 °C (solution in CD₂Cl₂): δ(¹H) 7.80 (d, *J* = 2.1) + 7.41* (s) (1 H total, ratio 1:3), 6.32 (d, *J* = 2.0) + 6.04 (d, *J* = 2.0) (1 H total, ratio 1:3), 2.45 (s) + 2.34 (s) (3 H total, ratio 3:1).

[HB(pz)₃]₂Sn (3) was prepared from 0.53 g (2.8 mmol) of SnCl₂ and 1.40 g (5.6 mmol) of K[HB(pz)₃]¹ (30 mL of methylene chloride, 6 h stirring) to give 1.3 g (86%) of crude product. Traces of pyrazole were removed by sublimation under vacuum to leave a material of mp 162–165 °C. Anal. Calcd for C₁₈H₂₀B₂N₁₂Sn (*M_r* = 544.4): C, 39.67; H, 3.70; B, 3.98; N, 30.86; Sn, 21.79. Found: C, 39.39; H, 3.51; B, 3.70; N, 30.50; Sn, 21.63.

NMR data: δ(¹H) 7.69 (1 H, d, *J* = 2.2, of d, *J* = 0.6), 7.35 (1 H, d, *J* = 1.5), 6.17 (1 H, unsym t = two overlapping d, *J* = ca. 2.1); δ(¹¹B) −2.8 (d, *J* = 95); δ(¹³C) 140.3, 135.7, 104.9; δ(¹¹⁹Sn) −877 (s, *h*_{1/2} = 750 Hz; at −50 °C: *h*_{1/2} = 270 Hz).

$[\text{HB}(\text{pz}^*)_2]\text{Sn}$ (4, $\text{Hpz}^* = 3,5\text{-dimethylpyrazole}$).⁷ NMR data: $\delta(^1\text{H})$ 5.72 (1 H, s), 2.26 (3 H, s), 1.80 (3 H, s); $\delta(^{11}\text{B})$ -8.3 (broad s, $h_{1/2} = 320$ Hz); $\delta(^{13}\text{C})$ 148.9, 144.9, 106.0, 12.6, 12.3; $\delta(^{119}\text{Sn})$ -933 (s, $h_{1/2} = 350$ Hz; at -50°C : $h_{1/2} = 240$ Hz). Lit.:⁷ $\delta(^1\text{H})$ 5.79 (3 H, s), 4.75* (1 H, s), 2.33 (9 H, s), 1.85 (9 H, s); $\delta(^{119}\text{Sn})$ (solution in CD_2Cl_2) -935 (s, $h_{1/2} = 300$ Hz).

$[\text{HB}(\text{pz}^*)_3]\text{SnCl}^7$ (9) decomposes near 250°C . NMR data: $\delta(^1\text{H})$ 5.82 (1 H, s), 2.50 (3 H, s), 2.37 (3 H, s); $\delta(^{11}\text{B})$ -9.6 (d, $J = 92$); $\delta(^{13}\text{C})$ 149.8, 145.4, 106.3, 13.8, 12.5; $\delta(^{119}\text{Sn})$ -579 ($h_{1/2} = 200$ Hz). Lit.:⁷ $\delta(^1\text{H})$ (solution in C_6D_6) 5.40 (1 H, s), 2.36 (3 H, s), 1.96 (3 H, s); $\delta(^{119}\text{Sn})$ (solution in CD_2Cl_2) -1460 (s, $h_{1/2} > 300$ Hz).

$[\text{H}_2\text{B}(\text{pz})_2]\text{Sn}$ (5) was prepared from 0.75 g (3.95 mmol) of SnCl_2 and 1.47 g (7.9 mmol) of $\text{K}[\text{H}_2\text{B}(\text{pz})_2]^1$ (30 mL of methylene chloride, 2 h stirring) to give 1.23 g (75%) of material, sintering at 110°C and decomposing at $116\text{--}124^\circ\text{C}$. The material could not be purified by recrystallization but deteriorated in all relevant attempts; it decomposes readily at elevated temperatures. Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{B}_2\text{N}_8\text{Sn}$ ($M_r = 412.4$): C, 34.92; H, 3.91; B, 5.24; N, 27.16; Sn, 28.77. Found: C, 32.89; H, 3.64; B, 4.40; N, 25.15; Sn, 30.29.

NMR data: $\delta(^1\text{H})$ 7.64 (1 H, d, $J = 1.7$), 7.36* (1 H, s), 6.21* (1 H, unresolved), ca. 4* (1 H); $\delta(^{11}\text{B})$ -8.7 (s, $h_{1/2} = 280$ Hz); $\delta(^{13}\text{C})$ 139.4, 136.5, 105.3; $\delta(^{119}\text{Sn})$ -654 (s, $h_{1/2} = 450$ Hz; at -50°C : $h_{1/2} = 150$ Hz).

$[\text{H}_2\text{B}(\text{pz})_2]\text{SnCl}$ (10) was obtained from 0.68 g (3.6 mmol) of SnCl_2 and 0.67 g (3.6 mmol) of $\text{K}[\text{H}_2\text{B}(\text{pz})_2]^1$ (20 mL methylene chloride, 2 h stirring); 0.8 g (74%), mp $142\text{--}144^\circ\text{C}$ dec. Anal. Calcd for $\text{C}_6\text{H}_8\text{BClN}_4\text{Sn}$ ($M_r = 301.1$): C, 23.92; H, 2.68; B, 3.59; Cl, 11.79; N, 18.60; Sn, 39.42. Found: C, 24.09; H, 2.50; B, 3.21; Cl, 12.30; N, 18.04; Sn, 39.17.

NMR data: $\delta(^1\text{H})$ 7.8* (1 H, s), 7.65 (1 H, d, $J = 1.5$), 6.35* (1 H, unsym t), 3.85* (1 H); $\delta(^{11}\text{B})$ -8.9 (t, $J = 98$); $\delta(^{13}\text{C})$ 138.7, 137.3, 106.2; $\delta(^{119}\text{Sn})$ -305 (s, $h_{1/2} = 1250$ Hz). At -50°C : $\delta(^{119}\text{Sn})$ -262 (small and broad), -336 (s, $h_{1/2} = 330$ Hz).

$[\text{H}_2\text{B}(\text{pz}')_2]\text{Sn}$ (7) was prepared from 1.08 g (5.7 mmol) of SnCl_2 and 2.44 g (11.4 mmol) of $\text{K}[\text{H}_2\text{B}(\text{pz}')_2]^{9,10}$ (30 mL of methylene chloride, 3 h stirring) to give 2.2 g (82%) of crude product. This

was redissolved in a minimal amount of methylene chloride and the clear solution was cooled to $-40\text{ }^{\circ}\text{C}$; the precipitated product decomposed at $122\text{--}124\text{ }^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{B}_2\text{N}_8\text{Sn}$ ($M_r = 468.5$): C, 40.98; H, 5.16; B, 4.61; N, 23.91; Sn, 25.34. Found: C, 41.15; H, 5.14; B, 4.51; N, 23.71; Sn, 25.43.

NMR data: $\delta(^1\text{H})$ 7.53 (1 H, d, $J = 1.8$), 5.98 (1 H, d, $J = 1.8$), 3.9* (1 H, ill-resolved q), 1.63 (3 H, s); $\delta(^{11}\text{B})$ -9.8 (unresolved t?, $h_{1/2} = 350\text{ Hz}$; ^1H decoupled: $h_{1/2} = 190\text{ Hz}$); $\delta(^{13}\text{C})$ 149.9, 136.8, 105.1, 11.7; $\delta(^{119}\text{Sn})$ -685 (s, $h_{1/2} = 360\text{ Hz}$).

$[\text{H}_2\text{B}(\text{pz}')_2]\text{SnCl}$ (12) was prepared from 1.13 g (5.96 mmol) of SnCl_2 and 1.28 g (5.96 mmol) of $\text{K}[\text{H}_2\text{B}(\text{pz}')_2]^{9,10}$ (30 mL of methylene chloride, 3.5 h stirring). The product, mp $144\text{--}146\text{ }^{\circ}\text{C}$ dec, precipitated on concentration of the solution and was obtained in 66% yield (1.3 g). Anal. Calcd for $\text{C}_8\text{H}_{12}\text{BClN}_4\text{Sn}$ ($M_r = 329.1$): C, 29.17; H, 3.68; B, 3.28; Cl, 10.79; N, 17.02; Sn, 36.06. Found: C, 29.65; H, 3.72; B, 3.31; Cl, 10.77; N, 16.80; Sn, 35.82.

NMR data: $\delta(^1\text{H})$ 7.49 (1 H, d, $J = 1.9$), 6.08 (1 H, d, $J = 1.5$), 3.9* (1 H, very broad), 2.52 (3 H, s); $\delta(^{11}\text{B})$ -9.9 (t, $J = 98$); $\delta(^{13}\text{C})$ 151.0, 137.6, 106.2, 13.2; $\delta(^{119}\text{Sn})$ -271 (s, $h_{1/2} = 365\text{ Hz}$).

$[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{Sn}$ (6) was prepared from 2.0 g (6.1 mmol) of $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]^8$ and 0.59 g (3.1 mmol) of SnCl_2 (30 mL of methylene chloride, 4 h stirring) to give 2.0 g (89%) of crude product. It was recrystallized from cyclohexane to give a material of mp $276\text{--}280\text{ }^{\circ}\text{C}$ dec. Anal. Calcd for $\text{C}_{36}\text{H}_{32}\text{B}_2\text{N}_8\text{Sn}$ ($M_r = 717.0$): C, 60.30; H, 4.50; B, 3.02; N, 15.63; Sn, 16.55. Found: C, 60.46; H, 4.44; B, 3.30; N, 15.92; Sn, 16.08.

NMR data: $\delta(^1\text{H})$ 7.58 (1 H, d, $J = 1.5$), 7.40 (1 H, d, $J = 1.2$), 7.25* (3 H, unresolved), 6.95* (2 H, very broad s), 6.19 (1 H, unsym t = two overlapping d, $J = \text{ca. } 1.9$); $\delta(^{11}\text{B})$ 1.3 (s, $h_{1/2} = 500\text{ Hz}$); $\delta(^{13}\text{C})$ 147*, 140.1, 137.7, 134.4, 127.7, 127.4, 104.2; $\delta(^{119}\text{Sn})$ -728 (s, $h_{1/2} = 75\text{ Hz}$).

$[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{SnCl}$ (11) was obtained from 1.0 g (5.3 mmol) of SnCl_2 and 1.78 g (5.27 mmol) of $\text{K}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]^{11}$ (30 mL of methylene chloride, 2 h stirring). The crude material (2.2 g, 92%) was purified by recrystallization from toluene to give a product of mp $234\text{--}238\text{ }^{\circ}\text{C}$ dec. Anal. Calcd for $\text{C}_{18}\text{H}_{16}\text{BClN}_4\text{Sn}$ ($M_r = 435.1$): C, 47.67; H, 3.56; B, 2.38; Cl, 7.83; N, 12.36; Sn, 26.20. Found: C, 47.73; H, 3.41; B, 2.60; Cl, 7.70; N, 12.29; Sn, 26.22.

NMR data: $\delta(^1\text{H})$ 7.94 (1 H, d, $J = 2.1$), 7.68 (1 H, d, $J = 2.4$), 7.33* (4 H, unresolved), 6.60* (1 H, unresolved), 6.40 (1 H, unsym t = two overlapping d, $J = 2.3$); $\delta(^{11}\text{B})$ 1.5 (s, $h_{1/2} = 225$ Hz); $\delta(^{13}\text{C})$ 139.9, 139.0, 135.7*, 135.6*, 128.3*, 105.4; $\delta(^{119}\text{Sn})$ -353 (s, $h_{1/2} = 160$ Hz).

Results and Discussion

Preparation of Tin(II) Poly(1-pyrazolyl)borates and General Remarks. Several Sn(II) poly(1-pyrazolyl)borates of the types L_2Sn and LSnCl have been prepared by reaction of SnCl_2 with an alkali metal poly(1-pyrazolyl)borate. The compounds include the species L_2Sn where $\text{L} = [\text{B}(\text{pz})_4]^-$ (1), $[\text{B}(\text{pz}'_4)]^-$ (2), $[\text{HB}(\text{pz})_3]^-$ (3), $[\text{R}_2\text{B}(\text{pz})_2]^-$ ($\text{R} = \text{H}$ (5), C_6H_5 (6)), or $[\text{H}_2\text{B}(\text{pz}'_2)]^-$ (7) and LSnCl where $\text{L} = [\text{B}(\text{pz})_4]^-$ (8), $[\text{H}_2\text{B}(\text{pz})_2]^-$ (10), $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]^-$ (11), or $[\text{H}_2\text{B}(\text{pz}'_2)]^-$ (12) ($\text{Hpz} = \text{pyrazole}$, $\text{Hpz}' = 3\text{-methylpyrazole}$). All of these species were obtained by stirring a mixture of stoichiometric amounts of an alkali metal poly(1-pyrazolyl)borate and SnCl_2 in methylene chloride at room temperature. Species of the type LSnCl formed with particular ease, whereas prolonged reaction times were frequently required for the preparation of L_2Sn species. The two compounds L_2Sn (4) and LSnCl (9) with $\text{L} = [\text{HB}(\text{pz}^*)_3]^-$ ($\text{Hpz}^* = 3,5\text{-dimethylpyrazole}$) have previously been described and were prepared by this same route.⁷

The complexes derived from $\text{L} = [\text{H}_2\text{B}(\text{pz})_2]^-$ and those containing the 3-methylpyrazole moiety were extremely temperature sensitive and could not be recrystallized without apparent decomposition. Furthermore, many of the complexes, in particular those of the type LSnCl , underwent slow autogeneous changes even when stored in the solid state, much more readily in solution. For example, the complex $[\text{B}(\text{pz})_4]\text{SnCl}$ was also prepared and the ^1H NMR (and mass spectroscopic) data of a freshly prepared sample substantiated the formulation. However, even after a short period of time the spectrum had deteriorated and new signals emerged; no reliable ^{119}Sn NMR data could be obtained. Recent studies in our laboratory suggest that the noted deterioration of some of the complexes on standing is likely due to hydrolysis. It has been observed that alkali metal poly(1-pyrazolyl)borates are hygroscopic, a feature which has not been noted earlier. Thus, small amounts of water can be introduced into a system with the reagents. This may not necessarily interfere with the initial formation of the complexes but, obviously, can cause complications on storage. This feature may also explain the reported slow formation of pyrazole on standing of solutions of $[\text{HB}(\text{pz})_3]\text{Sn}(\text{CH}_3)_3$ in methylene chloride.⁴

The X-ray crystal structures of $[\text{HB}(\text{pz}^*)_3]_2\text{Sn}$ (**4**) and $[\text{HB}(\text{pz}^*)_3]\text{SnCl}$ (**9**) have been determined earlier. In the solid state **9** was found to have approximately trigonal bipyramidal geometry about tin (three N atoms, the Cl atom, and the lone pair), whereas the tin in **4** has an approximately octahedral environment (five N atoms and the lone pair). Hence, one of the pz^* groups of **4** was found to be different from the other five, which was not observed in the (room temperature) ^1H NMR spectrum (solution in CDCl_3).⁷ However, it has now been observed (by ^1H NMR) that in solution even at low temperature the equivalence of the six pz^* groups of **4** is maintained. This observation suggests that the solid state structure and the solution structure are not identical, since coordination of the $\text{Sn}(\text{II})$ to the six N atoms of equivalent pz^* groups give it an effective coordination sphere of seven, when the lone pair is included.

The arrangement of the following discussion is based on the assumption that in solution the $\text{Sn}(\text{II})$ will achieve the maximum coordination of a discrete molecule.

Tin(II) Poly(1-pyrazolyl)borates with Formal Coordination Number Seven. The room temperature ^1H (and ^{13}C) NMR spectrum of $[\text{B}(\text{pz})_4]_2\text{Sn}$ (**1**) exhibited only one set of signals for the pz groups. However, on cooling of **1** to -40°C , considerable line broadening of the ^1H NMR signals at 7.63 and 7.26 ppm occurred, whereas the signal at 6.32 ppm was essentially unaffected. New additional broad signals at about 6.8 and 7.9 ppm appeared near -70°C , and at -85°C two distinct sets of pyrazolyl signals with $\delta(^1\text{H})$ 7.93/6.81/6.38 (1 pz) and 7.59/7.40/6.38 (3 pz), respectively, were observed, indicating the presence of two different types of pz groups in 1:3 ratio. Hence, the species is fluxional in solution at room temperature, but the low-temperature ^1H NMR data suggest that only six of the eight pyrazolyl groups in **1** are coordinated to tin. Under these circumstances the coordination sphere of tin comprises six N atoms and the lone pair. As expected, the ^{11}B NMR spectrum of **1** featured one sharp signal at 0.4 ppm, and $\delta(^{119}\text{Sn})$ was observed at -744 .

The ^1H NMR spectrum of $[\text{B}(\text{pz}')_4]_2\text{Sn}$ (**2**) exhibited the anticipated two sets of pz' signals in 1:3 ratio even at room temperature; they merged into a single set near 50°C . With the exception of that of **H(4)**, the room-temperature signals were extremely broad. Again, only one ^{11}B NMR and one ^{119}Sn NMR signal were observed and both were quite comparable to those of **1**.

The room temperature ^1H NMR spectrum of $[\text{HB}(\text{pz})_3]_2\text{Sn}$ (3) exhibited signals for only one type of pz groups and no additional signals emerged on lowering of the temperature to -95°C . This observation correlates well with the data obtained for 1, since the only difference between the compounds is the replacement of the terminal pz group (*i.e.*, the one which is not bonding to the Sn(II) in the static structure) by H. It suggests that in solution all three pz groups of the $\text{HB}(\text{pz})_3$ ligands in 3 are bonding with the tin, even at low temperatures. Also, as noted above, no new ^1H NMR signals emerged in the ^1H NMR spectrum of 4 at low temperatures. Hence, unless even at -95°C rapid (on the NMR time scale) fluxionality persists, the solution structure of 4 is different from that in the solid state.

Both 3 and 4 exhibited only one ^{11}B NMR signal and the ^{119}Sn chemical shift of 3 ($\delta -877$) is quite comparable to that reported for 4 ($\delta -935$).⁷ Furthermore, the ^{119}Sn NMR data of the species 1 to 4 are all very similar and fall in the range of about -750 to -950 ppm (see Table I). This suggests that in solution

Table I

the coordinative environment of the Sn(II) in these compounds is identical. Since the NMR data indicate the binding of a total of six N atoms of the ligands to the tin, the cited chemical shift range seems to reflect seven-fold coordination (when including the lone pair) for Sn(II) in these poly(1-pyrazolyl)borates.

Tin(II) Complexes with Formal Coordination Number Five. A maximum coordination sphere of five may be expected for complexes of the type $[\text{R}_2\text{B}(\text{pz})_2]_2\text{Sn}$ (R = non-coordinating substituents), which results from the binding of four N atoms of the ligands to the Sn(II) and the lone pair of the latter.

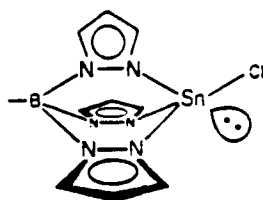
The compound $[\text{H}_2\text{B}(\text{pz})_2]_2\text{Sn}$ (5) was only obtained as crude (although, as based on ^1H NMR data, reasonably pure) material, which could not be purified by recrystallization or sublimation. Rather, all purification attempts resulted in deterioration of the sample and the formation of increasing amounts of free pyrazole was observed. The compound $[\text{H}_2\text{B}(\text{pz}')_2]_2\text{Sn}$ (7) could be somewhat purified by sacrificing yield.

Furthermore, the reaction of SnCl_2 with two molar equivalents of $\text{K}[(\text{C}_2\text{H}_5)_2\text{B}(\text{pz})_2]$ gave no pure identifiable product and there were indications (NMR spectra) that extensive ethyl group migration had occurred. In addition, the formation of substantial amounts of free pyrazole was observed, although all work was done under anhydrous conditions. On the other hand, when $\text{Na}[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]$ was employed in an analogous reaction, the desired $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]_2\text{Sn}$ (**6**) was obtained in good yield.

The ^{119}Sn chemical shifts of **5**, **6** and **7** were quite comparable with each other ranging from about -650 to -730 ppm. The broadness of the signal of **5** was somewhat disturbing; however, the signal sharpened considerably on lowering of the temperature. This feature may be due to conformational changes in these complexes with two puckered BN_4Sn rings, *i.e.*, containing the skeleton $\text{B}(\mu\text{-pz})_2\text{Sn}(\mu\text{-pz})_2\text{B}$.

In poly(1-pyrazolyl)borate complexes of $\text{Sn}(\text{II})$ of the type LSnCl , a maximum of three pyrazolyl groups can bind to the central metal atom if they are available. The room temperature ^1H NMR spectrum of $[\text{B}(\text{pz}')_4]\text{SnCl}$ (**8**) exhibited only one set of signals for the pz' groups. However, a second set began to emerge at -50°C , and at -70°C two sets of pz' signals in 1:3 ratio were clearly seen. This documents the expected binding of three N atoms of the ligand to the tin. The ^{11}B and the ^{119}Sn NMR spectrum of **8** exhibited only one signal each. On the other hand, the ^{119}Sn chemical shift, $\delta -533$, differed significantly from that reported⁷ for $[\text{HB}(\text{pz}^*)_3]\text{SnCl}$ (**9**) with $\delta -1460$. However, this latter datum is apparently in error: When the spectrum of freshly prepared **9** was recorded in CDCl_3 during the course of the present work, $\delta(^{119}\text{Sn})$ was observed at -579 .

It is apparent from the NMR data that the coordination of Sn in the compounds **8** and **9** in solution is the same and most likely to be five-fold: three N atoms of the ligands, one Cl atom, and the lone pair, as is illustrated in structure A. The ^{119}Sn chemical shifts of the compounds fall in the range between those of compounds of types **1** to **4** (with a presumably higher coordination of the Sn) and those of **5** to **7** (with different ligands surrounding the Sn). Apparently, the ^{119}Sn chemical shift range of about -530 to -730 ppm seems to reflect five-fold coordination about the $\text{Sn}(\text{II})$ in these poly(1-pyrazolyl)borate species.



A

Species with Formal Coordination Number Four. Finally, the species $[\text{H}_2\text{B}(\text{pz})_2]\text{SnCl}$ (**10**), $[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{SnCl}$ (**11**) and $[\text{H}_2\text{B}(\text{pz}')_2]\text{SnCl}$ (**12**) were examined. In all of these the tin of discrete species should be in four-coordinate environment, *i.e.*, bonded with two N atoms from the poly(1-pyrazolyl)borate moiety and the Cl atom, in addition to the lone pair. The ^{119}Sn chemical shifts of these three species fall in a fairly narrow range from about -270 to -350 ppm. This is not surprising considering the cited environment of the Sn(II). On the other hand, the signal of **10** seemed to be exceedingly broad as compared to those of **11** and **12**. However, when lowering the temperature the ^{119}Sn NMR signal of **10** began to split, and at -40°C two separate signals at -262 and -336 ppm, respectively, were observed. It is reasonable to assume that both signals indicate the same coordination sphere for the Sn(II). This can be explained by assuming that the puckered BN_4Sn ring of **10** (structure B) readily inverts at room temperature thus causing the broadness of the signal, whereas at low



B

temperature two structures of different geometries are frozen out. Such an inversion may be impaired by the methyl groups of the ligand in **12** and by a relatively large phenyl group in **11**.

Conclusion. As based on the preceding data, ^{119}Sn NMR spectroscopy seems to be a useful probe for the determination of the coordination sphere of Sn(II) in poly(1-pyrazolyl)borate complexes in solution. However, it should be emphasized that the solution structures are not necessarily identical with those in the solid state, as is seen in the case of compound 4.

Acknowledgment. This work was supported by the Office of Naval Research (K. N.).

References

- (1) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177.
- (2) Niedenzu, K.; Trofimenko, S. *Top. Curr. Chem.* **1986**, *131*, 1–37.
- (3) Nicholson, B. K. *J. Organomet. Chem.* **1984**, *265*, 153–157.
- (4) Lee, S. K.; Nicholson, B. K. *J. Organomet. Chem.* **1986**, *309*, 257–265.
- (5) Lobbia, G. L.; Bonati, F.; Cecchi, P.; Cingolani, A.; Lorenzotti, A. *J. Organomet. Chem.* **1989**, *378*, 139–146.
- (6) Zaidi, J. A. A.; Hashni, A. A.; Siddiqui, K. S. *J. Chem. Res. (S)* **1988**, 410–411.
- (7) Cowley, A. H.; Geerts, R. L.; Nunn, C. M.; Carrano, C. J. *J. Organomet. Chem.* **1988**, *341*, C27–C30.
- (8) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 6288–6294.
- (9) Niedenzu, K.; Niedenzu, P. M.; Warner, K. R. *Inorg. Chem.* **1985**, *24*, 1604–1606.
- (10) McCurdy, W. H. *Inorg. Chem.* **1975**, *14*, 2292–2294.
- (11) Layton, J. W.; Niedenzu, K.; Niedenzu, P. M.; Trofimenko, S. *Inorg. Chem.* **1985**, *24*, 1454–1457.

Table I. ^{119}Sn chemical Shift Data of Sn(II) Poly(1-pyrazolyl)borates (Hpz pyrazole, $\text{Hpz}' = 3\text{-methylpyrazole}$, $\text{Hpz}^* = 3,5\text{-dimethylpyrazole}$; solvent: CDCl_3)

Nr.	Compound	$\delta(^{119}\text{Sn})$	$h_{1/2}$	presumed coordination sphere of tin
1	$[\text{B}(\text{pz})_4]_2\text{Sn}$	-744	50	7
2	$[\text{B}(\text{pz}')_4]_2\text{Sn}$	-808	50	7
3	$[\text{HB}(\text{pz})_3]_2\text{Sn}$	-877	750 ^a	7
4	$[\text{HB}(\text{pz}^*)_3]_2\text{Sn}^b$	-933	350 ^a	7
5	$[\text{H}_2\text{B}(\text{pz})_2]_2\text{Sn}$	-654	450 ^a	5
6	$[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]_2\text{Sn}$	-728	75	5
7	$[\text{H}_2\text{B}(\text{pz}')_2]\text{Sn}$	-685	360	5
8	$[\text{B}(\text{pz}')_4]\text{SnCl}$	-533	230	5
9	$[\text{HB}(\text{pz}^*)_3]\text{SnCl}^c$	-579	200	5
10	$[\text{H}_2\text{B}(\text{pz})_2]\text{SnCl}$	-305	1250 ^d	4
11	$[(\text{C}_6\text{H}_5)_2\text{B}(\text{pz})_2]\text{SnCl}$	-353	160	4
12	$[\text{H}_2\text{B}(\text{pz}')_2]\text{SnCl}$	-271	365	4

^a $h_{1/2}$ narrows at lower temperature. — ^bLit.:⁷ $\delta(^{119}\text{Sn}) -935$ ($h_{1/2} = 300$ Hz) in CH_2Cl_2 . — ^cLit.:⁷ $\delta(^{119}\text{Sn}) -1460$ ($h_{1/2} = >300$ Hz) in CH_2Cl_2 . This datum seems to be in error. — ^dAt low temperatures the signal splits into two with $\delta -262$ and -336 , respectively.

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Doua Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code L52 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		

ORGANOELEMENT CHEMISTRY - Distribution List

Professor O. T. Beachley, Jr.
Department of Chemistry
State University of New York
Buffalo, NY 14214

Dr. Duncan Brown
Advanced Technology Materials, Inc.
520-B Danbury Road
New Milford, CT 06776

Professor Herbert C. Brown
Department of Chemistry
Purdue University
West Lafayette, IN 47907

Professor Steven L. Buchwald
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, MA 02139

Professor N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Professor William E. Hatfield
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. Kelvin T. Higa
Chemistry Division
Research Department
Naval Weapons Center
China Lake, CA 93555

Professor Robert H. Neilson
Department of Chemistry
Texas Christian University
Fort Worth, TX 76843

Professor Richard L. Wells
Department of Chemistry
Duke University
Durham, NC 27706